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# ON THE RELATION BETWEEN THE RADIOACTIVITY AND THE COMPOSITION OF THORIUM AND URANIUM MINERALS

A DISSERTATION

SUBMITTED TO THE FACULTY OF THE OGDEN GRADUATE SCHOOL OF SCIENCE IN CANDIDACY FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

DEPARTMENT OF CHEMISTRY.

By WILLIAM HORACE ROSS.

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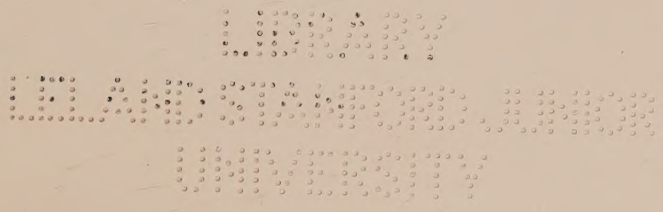

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# ON THE RELATION BETWEEN THE RADIOACTIVITY AND THE COMPOSITION OF THORIUM AND URANIUM MINERALS.

## PART I.

### *Thorium Compounds.*

It has been shown by McCoy[1] that, when account is taken of the absorption of the $\alpha$-particles, the specific radioactivity[2] of any pure uranium compound is proportional to the uranium content of the substance. This result was confirmed by Goettsch,[3] who worked in this laboratory on an additional number of pure uranium compounds. It has been shown[4] that a proportionality likewise exists in the case of uranium minerals, free from thorium, between the specific activity of the mineral and the percentage of uranium contained in it. In the case of the minerals, however, the ratio of specific activity to uranium content was found to be 4.15 times as great as for the pure compounds. The excess of activity of the ores is due to radium and its active products. Since the ratio of radium to uranium in minerals is always found to be a constant, this is considered good evidence that radium is a transformation product of uranium.

The work herein described was undertaken with a view to making a corresponding study in the case of thorium minerals. The importance of an investigation of this kind is evident on account of the many conflicting statements in the literature respecting the radioactivity of thorium and its different minerals. Schmidt,[5] Strutt,[6] and Mme. Curie,[7] have reported that all the thorium minerals examined by them show radioactive properties. In contradiction to this, it was announced by Hofman and Zerban[8] that an inac-

[1] Ber. d. chem. Ges., **37**, 2641, (1904). J. Amer. Chem. Soc., **27**, 391, (1905).

[2] The specific activity of a radio-active substance is the total activity of 1 gram of the substance expressed in terms of the activity due to 1 sq. cm. of a film of uranium oxide sufficiently thick to be of maximum activity. As this standard may be reproduced without difficulty when desired, and always with constant activity, it was used as being the most rational standard for the comparison of radio-active compounds.

[3] J. Am. Chem. Soc., **28**, 1548, (1906).

[4] McCoy, Phil. Mag., [6], **10**, 176, (1906).

[5] Ann. d. Phys., **65**, 141. (1898).

[6] Proc. Roy. Soc Lond., **76**, 88 and 312, (1905).

[7] Compt. Rend., **126**, 1101, (1898).

[8] Ber. d. chem. Ges., **35**, 531, (1902).

tive thorium preparation had been prepared by them from a Brazilian Monozite sand, and that thoria separated from certain minerals as, cleveite, samarskite, etc., although active when first prepared, had lost its activity some months after its removal from the ore. Baskerville and Zerban[1] also claimed to have prepared inactive thorium from a mineral found in South America.

From their study of thorium compounds Rutherford and Soddy[2] concluded that commercial thorium nitrate and the purest thorium nitrate, both give rise to the same amount of thorium emanation. Hahn and Ramsay[3] on the other hand were able to extract from the mineral thorianite a radioactive preparation several thousand times more active than thorium itself, and which gave rise to a proportionally larger amount of thorium emanation. This radio active product called "radiothorium," was shown to precede ThX in this series of radioactive products. The question, however, as to whether or not thorium itself is the first member of the series, or acquires its activity from the presence of a small amount of radiothorium accidentally mixed with it, was still left an open one.

*The methods of determining the specific activity of thorium compounds.*

All the thorium minerals which were studied in this research contained uranium, though often in very small quantities. This made it necessary to determine the percentage of uranium in each mineral in order to allow for the uranium activity. The specific activity of uranium in pure compounds was found by McCoy and Goettsch[4] to be 790, while the corresponding value for minerals was found to be 3280, or 4.15 times as great. Knowing the percentage of uranium in a thorium mineral, the activity due to uranium and its products can therefore be calculated. This, subtracted from the total activity of the mineral, gives the activity due to the thorium in the mineral. When this was done, it was found, as was observed for the uranium minerals, that that part of the activity due to thorium and its products in the mineral was in every case proportional to the percentage of thorium contained in it.

[1] J. Am. Chem. Soc., **26**, 1642, (1904).
[2] Proc. Chem. Soc , **18**, 120 (1902).
[3] J. de Chim Phys.. **38**, 3371 and **3**, 617, (1905)
[4] J. Am Chem. Soc., **28**, 1556, (1906).

For the determination of the total radioactivity of a uranium compound, two methods have been employed.[1] Each of the two methods involves the quantitative measurement of the activity of thin films of the substance of known weight, varying from about 1 to 20 mg. per sq. cm. Films weighing 20 mg. per sq. cm. show maximum activity. One of the methods[2] consists in finding the values of the ratio $\frac{w}{a}$ for thin films of various weights, where $w$ is the weight of the film, and $a$ its observed activity in terms of the unit defined above. By graphic extrapolation, the value of this ratio for an infinitely thin film may be found. This limiting value of the ratio is designated as $\left(\frac{w}{a}\right)_0$. In the case of an infinitely thin film, $a = \frac{1}{2} k_1 w$, where $k_1$ is the total activity of unit weight of the thin film. The factor $\frac{1}{2}$ is used since half of the rays are directed downward and are therefore absorbed by the metal plate carrying the film. Hence, the total activity, $k_1$, of unit weight of a compound is $k_1 = 2/\left(\frac{w}{a}\right)_0$. By definition $k_1$ is the specific activity.

*The correction to be applied to the observed specific activity of the evolved emanation.*

When applying this method to the determination of the total activity of thorium compounds, the method of procedure is more complicated than in the case of uranium compounds, owing to the fact that the former give rise to a gaseous emanation, the activity of which is considerable compared with that of the solid film. This is particularly noticed when measurements are made with the heavier films, since the absorption of the emanation by the film itself does not take place to the same extent as occurs in the case of the $\alpha$-rays. Hence, the observed activity of the thicker films of thorium compounds must be corrected for the effect of the emanation. This was done by the method developed by McCoy and Ross.[3] The proper amount of the compound to be investigated was ground up finely with alcohol in an agate mortar, and then transferred to a small beaker. The beaker was rotated rapidly to bring the particles into suspension and the mixture then poured quickly into a circular

[1] McCoy, J. Am. Chem., Soc., **27**, 391, (1905).
[2] McCoy, loc. cit.
[3] Am. J. Sci., **21**, 433, (1906).

shallow tin dish, having an area of 39.8 sq. cm. The alcohol was allowed to evaporate under a bell-jar which inclosed also some calcium chloride. Each film prepared in this way, and carefully weighed, was placed in the electroscope case and its activity measured after being allowed to remain in the case five minutes in order to permit the maximum amount of emanation to accumulate. After several observations were made, in order to obtain a true average, the electroscope was again charged, and, as soon as the leaf had reached the beginning of the scale in the subsequent discharge, the film was rapidly withdrawn from the case by means of a thread. The small door of the case opened and closed automatically. At the instant of removing the film, the position of the leaf on the scale was noted, and the stop-watch was started. The leaf continued to move with gradually decreasing velocity for about five minutes, at the end of which period the emanation had almost completely decayed, and the motion of the leaf became very slow and uniform, corresponding to the natural leak of the instrument.

If $D$ be the number of divisions of the scale traversed by the leaf in five minutes, corrected for the natural leak, and $E$ the initial activity of the evolved emanation, then it was shown[1] that $E = .173\ D$. $E$ is small except for the thicker films. Now the observed activity, $a_1$, of a thorium film is too great on account of the activity, $E$, of the evolved emanation. But the value $a_1 - E$, which represents the activity of the solid film alone, is too small because the film has lost a fraction of its emanation and ThB. This loss of activity is equal to $2\ E$, since the activity of ThB is approximately equal to that of the emanation when present in equilibrium amount. The total activity of the film is $k_1 w$. Therefore the fraction of the total activity lost by the film is $\frac{2\ E}{k_1\ w}$, and the fraction remaining, $1 - \frac{2\ E}{k_1\ w}$. But the observed activity of this fraction is $a_1 - E$. Therefore the true activity, $a$, of the film, if none of the emanation were evolved, is

$$a = \frac{a_1 - E}{1 - \frac{2\ E}{k_1\ w}}$$

[1] McCoy and Ross, loc. cit.

*The specific activity of thorium dioxide.*

The first compound to be investigated was thorium dioxide. This was prepared from Kahlbaum's purest thorium nitrate by heating at first cautiously, and then strongly in the blast. The purity of the nitrate was established by the analysis of a solution made by dissolving 4 grams in 250$^{cc}$ of water. 25$^{cc}$ evaporated to dryness in a large platinum crucible, and ignited, gave a residue weighing 0.1750 gram. Portions of 25$^{cc}$ diluted and then precipitated with ammonia gave upon ignition 0.1746 and 0.1748 gram. Finally, portions of 25$^{cc}$ analysed by Neish's[1] method, gave 0.1751 and 0.1754 gram. The agreement of the weight of the thorium dioxide obtained by the direct evaporation of the nitrate solution with the amount obtained after precipitation of the thorium shows the oxide to be free from any appreciable amount of non-volatile impurities. Before any activity measurements were made, the oxide was allowed to stand over a month in order that it might attain its maximum activity.

Table I gives the results obtained with very thin films of sample *A* of pure thorium dioxide without any correction being applied for effect of the emanation. $w$ is the weight of the film; $a_1$ the observed activity of the film in terms of the unit of activity. If the time of discharge[2] of the electroscope through a given range of the scale is $\theta$ for the film, and $\theta_s$ for the standard film of uranium oxide which had and area of 39.8 sq. cm., then the observed activity of the film is $a_1 = \frac{39{\cdot}8\,\theta_s}{\theta}$

TABLE I.—*Thorium dioxide.*

| $w$ | $a_1$ | $\frac{w}{a_1}$ |
|---|---|---|
| ·2798 | 41·36 | ·00676 |
| ·2020 | 30·80 | ·00599 |
| ·1026 | 20 70 | ·00495 |
| ·0546 | 12·27 | ·00444 |

$$\left(\frac{w}{a_1}\right)_0 = {\cdot}00387$$

The curve obtained by plotting the values of $\frac{w}{a_1}$ as ordinates and the corresponding values of $w$ as abscissæ is nearly a straight

[1] J. Am Chem. Soc., **26**, 780, (1904).
[2] Corrected for natural leak.

line. The intercept on the axis of ordinates of the prolongation of the curve gave the value of the ratio $\frac{w}{a_1}$ for an infinitely thin film. The value so found is designated in the table as $\left(\frac{w}{a_1}\right)_0$. Since it has been shown that the specific activity, $k_1$, of a radioactive compound is given by the equation, $k = 2/\left(\frac{w}{a_1}\right)_0$, therefore, the specific activity of sample A, as determined without taking into account the effect of the evolved emanation, is equal to $\frac{2}{\cdot 00387} = 517$.

That this value approximates very closely the true specific activity of the compound follows from the conclusion drawn by McCoy and Ross,[1] who showed theoretically that in the case of a very thin film of thorium compound, the actual activity of the evolved emanation exactly compensates for the deficiency of activity of the solid film, and that therefore the observed activity of such a film is equal to its true activity. Owing to the difficulty of preparing very thin films of different weights all equally uniform, this value of $k_1$, instead of being taken as the true specific activity of sample $A$, was used in determining the correction to be applied to the observed activity, $a_1$, when measurements were made of the activities of thicker films. Thus, the true activity of such films $= \frac{a_1 - E}{1 - 2E} = a$

$517w$

Table II gives the results obtained with films of sample A of varying weights.

TABLE II.—*Thorium dioxide.*

| $w$ | $a_1$ | $a$ | $\frac{w}{a}$ | $E$ | $\frac{w}{E}$ |
|---|---|---|---|---|---|
| 1·8893 | 58·80 | 56·90 | ·03322 | 2·17 | ·87 |
| ·9182 | 55·60 | 54·70 | ·01678 | 1·20 | ·77 |
| ·2798 | 41·36 | 41·00 | ·00683 | ·43 | ·65 |
| ·2020 | 33·80 | 33·66 | ·00600 | ·35 | |
| ·1026 | 20·70 | 20·66 | ·00496 | ·18 | |
| ·0546 | 12·27 | 12·26 | ·00445 | .09 | |
| | $\left(\frac{w}{a_1}\right)_0 = \cdot 00387$ | | | $\left(\frac{w}{E}\right)_0 = \cdot 58$ | |

[1] Loc. cit

For the lighter films, $E$ was too small to be measured directly. From the curve obtained by plotting the values of the ratio $\frac{w}{E}$ for the heavier films as ordinates and the corresponding values of $w$ as abscissæ, in the same way as described for the values obtained in Table I, the value of the ratio $\frac{w}{E}$ for an infinitely thin film may be found. Then, since $E = w/\left(\frac{w}{E}\right)_0$, the value of $E$ for any particular film may be determined. $E$ was calculated in this way for the three lightest films in Table II. A new curve plotted from the results given Table II, in the same way as was done for the values in Table I, gave for $\left(\frac{w}{a}\right)_0$ the same value as before. Therefore, the true specific activity of sample $A$ is 517.

The specific activity of a radioactive compound may also be determined in another way. It was shown by McCoy[1] that $k_2 = \frac{2{\cdot}303\ s}{w} \log \frac{1}{1-x}$, where $k_2$ is the absorption co-efficient for unit weight on unit area; $s$ the area of each film, 39.8 sq. cm.; and $x$ is the ratio of the observed activity of a thin film to that of a film of the same substance of equal area and sufficiently thick to be of maximum activity. In the case of sample $A$, such a film had an activity of 56.9 (Table II.) Therefore, $x$, for any particular film of the same compound is equal to the observed activity, $a_1$, divided by 56.9. The co-efficient of absorption, $k_2$, differs for different compounds, but is constant for any one compound.[2] For the sample $A$ of thorium dioxide, the mean value of $k_2$ was found to be 178. Then, since $k_1 = \frac{2\,k_2\,a}{s}$, therefore $k_1$ for sample $A = \frac{2 \times 178 \times 56{\cdot}9}{39{\cdot}8} = 509$. The mean value of $k_1$ for the two methods is 513. Thorium dioxide contains 87.9 per cent. of thorium. Therefore, the total activity of thorium together with its products in sample $A$ is $\frac{513}{{\cdot}879} = 584$.

[1] J. Am. Chem. Soc., **27**, 391, (1905).
[2] McCoy and Goettsch, loc cit.

*The analysis of thorium minerals.*

The activities of several thorium minerals were determined by the first method described in the same way as for sample *A* of pure thorium dioxide. The ore was ground up very finely in alcohol, and care was taken to prevent any segregation of the more active constituents of the ore in the preparation of the films. Sampled portions of the powdered ore were then taken for the purpose of determining the percentage of thorium and uranium present. The uranium was determined by reduction with zince in sulphuric acid and titration with potassium permanganate.[1] The analyses for thorium were made by the method of Neish.[2] Instead of evaporatin to dryness the solution obtained by dissolving the precipitated hydroxides in dilute nitric acid, this solution was almost neutralized by adding dilute ammonia, methyl orange being used as indicator. 250$^{cc}$ of a solution of meta-nitrobenzoic acid, made by dissolving 4 grams of the acid in a liter of water, was then added slowly with constant stirring. After being warmed to 80° for a time, the precipitate , which collected and settled to the bottom, was filtered off and washed with a 5 per cent. solution of the precipitant. The precipitate was then dissolved in dilute nitric acid, diluted to about 150$^{cc}$, almost neutralized with dilute ammonia as before, and the thorium then reprecipitated by the addition of 200$^{cc}$ more of the nitrobenzoic acid solution. By this procedure, which shortened somewhat the method outlined by Neish, pure white thorium dioxide, giving very concordant results, was always obtained.

The locality of origin, and the percentage of thorium and uranium in the minerals investigated are shown in Table III.

TABLE III.—*Thorium Minerals.*

| No. | Mineral. | Per cent. Thorium. | Uranium. |
|---|---|---|---|
| 1. | Orangite, Langesundsfjord, Norway ..... | 43·1 | 7·76 |
| 2. | Thorite " " ..... | 46·6 | 6·26 |
| 3. | Monazite, McDowell Co., N. C..... | 5·27 | ·33 |
| 4. | " Roada, Norway ..... | 15·18 | ·46 |
| 5. | " Commercial sample..... | 2·72 | ·12 |

[1] The details of the method of separation and determination of uranium are given in Part II.

[2] Loc. cit.

*The specific activity of thorium minerals.*

The activity of films of thorium minerals was corrected for the effect of the emanation according to the formula applied to films of pure thorium dioxide. In calculating $a$ from $a_1$, the approximate value of $k_1$, as found from the uncorrected activity of the thinner films, was used. This procedure involves no appreciable error in the calculation of the true activity.

The results are given in Tables IV to VIII. The significance of the symbols is the same as given under sample *A*. The curves for all the minerals were smooth. It is not necessary to reproduce them here.

TABLE IV.—*Orangite, No. 1.*

| $w$ | $a_1$ | $a$ | $\frac{w}{a}$ | $E$ |
|---|---|---|---|---|
| 1·2400 | 52·29 | 47·2 | ·02628 | 5·80 |
| ·3415 | 45·01 | 44·1 | ·00775 | 1·50 |
| ·2259 | 39·24 | 38·8 | ·00583 | 1·00 |
| ·1212 | 28·46 | 28·3 | ·00428 | (·55) |
| ·0526 | 14·85 | 14·8 | ·00355 | (·24) |
| | $\left(\frac{w}{a}\right)_0$=·00310 | | $\left(\frac{w}{E}\right)_0$=·22 | |

TABLE V.—*Thorite, No. 2.*

| $w$ | $a_1$ | $a$ | $\frac{w}{a}$ | $E$ |
|---|---|---|---|---|
| 1·1825 | 50·51 | 47·1 | ·02511 | 3·90 |
| ·3243 | 43·03 | 42·4 | ·00765 | 1·16 |
| ·2339 | 39·37 | 39·0 | ·00600 | ·88 |
| ·1349 | 29·74 | 29·6 | ·00456 | (·53) |
| ·0904 | 22·61 | 22·6 | ·00400 | (.34) |
| | $\left(\frac{w}{a}\right)_0$=·00301 | | $\left(\frac{w}{E}\right)_0$=·26 | |

TABLE VI.—*Monazite, No. 3.*

| $w$ | $a_1$ | $a$ | $\frac{w}{a}$ | $E$ |
|---|---|---|---|---|
| 1·0587 | 4·70 | 4·55 | ·2330 | .17 |
| ·2825 | 3·96 | 3·94 | ·0717 | .04 |
| ·2059 | 3·43 | 3·42 | ·0602 | .03 |
| ·1094 | 2·36 | 2·35 | ·0466 | (.02) |
| ·0476 | 1·23 | 1·23 | ·0387 | (.01) |
| | $\left(\frac{w}{a}\right)_0$=·0332 | | $\left(\frac{w}{E}\right)_0$=6·2 | |

TABLE VII.—*Monazite, No. 4.*

| $w$ | $a_1$ | $a$ | $\frac{w}{a}$ | $E$ |
|---|---|---|---|---|
| 1.1081 | 12·83 | 12·27 | 0903 | ·64 |
| ·2973 | 10·75 | 10·64 | 0279 | ·17 |
| ·2123 | 9·53 | 9·48 | ·0224 | ·12 |
| ·1078 | 6·26 | 6·24 | ·0173 | (·06) |
| ·0526 | 3·68 | 3·67 | ·0143 | (·03) |

$\left(\frac{w}{a}\right)_o = ·0122$ $\qquad$ $\left(\frac{w}{E}\right)_o = 1·7$

TABLE VIII.—*Monazite, No. 5.*

| $w$ | $a_1$ | $a$ | $\frac{w}{a}$ | $E$ |
|---|---|---|---|---|
| 1·0590 | 2·15 | $a$ is practically equal to $a_1$. | ·493 | Too small to be accurately measured. |
| ·3174 | 1·89 | | ·168 | |
| ·2156 | 1·70 | | ·127 | |
| ·1375 | 1·37 | | ·100 | |
| ·1170 | 1·25 | | ·094 | |
| ·0785 | ·89 | | ·088 | |
| ·0348 | ·46 | | ·076 | |

$\left(\frac{w}{a}\right)_o = ·066$

In Table IX, $k_{1m}$ represents the specific activity of the mineral as calculated from $k_{1m} = 2/\left(\frac{w}{a}\right)_o$. $k_{1U}$ represents the activity due to uranium and its products contained in 1 gram of the mineral. This is found by multiqlying the weight of uranium in 1 gram of the mineral by 3280; since, as has been mentioned, the specific activity of a thorium free mineral containing 1 gram of uranium is 3280 units. $k_{1Th}$ is the difference between $k_{1m}$ and $k_{1U}$; it represents the activity due to thorium and its products in 1 gram of the mineral. In the last column $P_{Th}$ is the weight of thorium in 1 gram of the mineral. $\frac{k_{1Th}}{P_{Th}}$ is as nearly constant as one could reasonably expect, considering that all the errors of experiment are accumulated on this ratio. It may be concluded, therefore, that the specific radioactivity due to 1 gram of thorium in any mineral is a constant, and is equal to 953 units. The radioactivity of any mineral containing uranium and thorium which is sufficiently old geologically, is therefore equal to $3280\ P_U + 953\ P_{Th}$.

TABLE IX.—*Thorium Minerals.*

| No. | Name. | %Th | %U | $k_{1m}$ | $k_{1U}$ | $k_{1Th}$ | $\frac{k_{1Th}}{P_{Th}}$ |
|---|---|---|---|---|---|---|---|
| 1. | Orangite..... | 43·10 | 7.76 | 649 | 255 | 394 | 914 |
| 2. | Thorite..... | 46·60 | 6·26 | 664 | 205 | 459 | 985 |
| 3. | Monazite..... | 5·27 | ·33 | 60·2 | 10·9 | 49·3 | 935 |
| 4. | " ..... | 15·18 | ·46 | 164 | 15 | 149 | 982 |
| 5. | " ..... | 2 72 | ·12 | 29·8 | 4·0 | 25·8 | 950 |

Mean = 953

The fact that the specific activity of thorium in minerals is found to be constant makes it necessary to assume that the activity of thorium is not due to radioactive bodies accidentally retained by the thorium (as radium frequently is by barium sulphate), but that radiothorium is a disintegration product of ordinary thorium with a relatively slow period.

*The specific activity of thorium in thorium dioxide recently extracted from thorium minerals.*

In the analyses of the minerals, the thorium was weighed as dioxide. This was very pure chemically. During the course of the analysis, the thorium was precipitated once by oxalic acid, once by potassium hydroxide, and twice by meta-nitrobenzoic acid. The thorium residues from each of the minerals were kept separate, and made into films. Measurements were made of the activities of the films one month later. The thorium dioxide then contained the maximum amounts of Th X, Emanation, Th A and Th B. The results are given in Tables X to XII, which represent the samples of dioxide prepared from the minerals, No. 1, No. 2 and No. 4 respectively. A summary is given in Table XIII.

TABLE X.—*Thorium dioxide—B.*

| $w$ | $a_1$ | $a$ | $\frac{w}{a}$ | $E$ |
|---|---|---|---|---|
| ·2267 | 61·4 | 60·9 | ·0372 | 1 04 |
| ·1170 | 40·2 | 40 1 | ·00292 | (·50) |
| ·0673 | 25·1 | 25 1 | 00268 | (·30) |

$$\left(\frac{w}{a}\right)_0 = ·00213$$

TABLE XI—*Thorium dioxide—C.*

| $w$ | $a_1$ | $a$ | $\frac{w}{a}$ | $E$ |
|---|---|---|---|---|
| ·2634 | 68·2 | 67·8 | ·00389 | 1·04 |
| ·1292 | 41·8 | 41·7 | ·00310 | (·50) |
| ·0657 | 24·1 | 24·1 | ·00273 | (·20) |

$$\left(\frac{w}{a}\right)_0 = ·00230$$

TABLE XII.—*Thorium dioxide—D.*

| $w$ | $a_1$ | $a$ | $\frac{w}{a}$ | $E$ |
|---|---|---|---|---|
| ·2088 | 57·6 | 57·2 | ·00365 | 1·10 |
| ·1083 | 35·9 | 35·7 | ·00303 | (·60) |
| ·0585 | 21·6 | 21·5 | ·00272 | (·30) |

$$\left(\frac{w}{a}\right)_0 = ·00240$$

TABLE XIII.—*Thorium dioxide.*

| Sample | Source | $\left(\frac{w}{a}\right)_0$ | $k_1$ | $\frac{k_1}{P}$ |
|---|---|---|---|---|
| A | Thorium Nitrate..... | ·00387 | 517 | 588 |
| B | Orangite No. 1..... | ·00243 | 823 | 936 |
| C | Thorite No. 2..... | ·00230 | 870 | 989 |
| D | Monazite No. 4..... | ·00240 | 833 | 948 |
| | | | | 958 |

Mean of B, C and D = 958

P represents the weight of thorium in 1 gram of the oxide. The mean value of $\frac{k_1}{P}$ for the last three samples is 958, which represents the total activity of 1 gram of thorium in the oxide. The corresponding value for thorium in the minerals is 953. Since the activity of thorium in samples B, C and D, and in minerals is practically identical, it follows that no appreciable fraction of the radiothorium present in the minerals has been removed by the processes of analysis. The oxides obtained from the commercial thorium salts, *e. g.*, sample A, are however only a little more than one-half as active as the oxides contained in, or separated from, the natural thorium minerals.

*On the separation of radiothorium from thorium.*

The least active thorium compound described, sample A, gave off an appreciable amount of emanation. It must, therefore, have contained a considerable portion of the equilibrium amount of radiothorium, which may be symbolized Rt. I have attempted by a number of methods to remove the radiothorium completely and so obtain thorium of minimum activity. The experiments carried out and the results obtained may now be described.

It was first shown by Rutherford and Soddy[1] that Th X and subsequent products may be removed from a compound of thorium in solution by repeating a few times the precipitation of the thorium by ammonia. By this treatment the Th X passes into the filtrate, and the activity of the thorium compound is thereby greatly reduced. In the course of five or six weeks, however, in Rutherford and Soddy's experiments, the activity seemed to be completely regained, owing to the reproduction of Th X, etc. To ascertain if any of the radiothorium was removed by precipitation with ammonia, a quantity of thorium nitrate from the same lot from which sample A had been made, was precipitated with ammonia. The precipitated hydroxide was filtered off, dissolved in dilute nitric acid, and the process repeated 100 times. The last precipitate was ignited to thorium dioxide, and its activity determined immediately and at intervals throughout a period of several weeks. The specific activity at first showed a minimum value of $k_1 = 185$. The activity increased and reached a maximum at the end of five weeks when $k_1 = 453$. The result shows that some of the radiothorium had been removed, since the value of $k_1$ found for sample A was 513. That a considerable amount of radiothorium still remained, however, was shown by the fact that the minimum activity increased at a rate which indicated the production of Th X and subsequent products.

Another portion of the nitrate solution containing 10 grams of salt was treated with 40$^{cc}$ of a 3 per cent. solution of hydrogen peroxide. The precipitated thorium was separated from the filtrate by a Pukall filter. The precipitate was dissolved in 15$^{cc}$ of concentrated nitric acid, diluted and partly neutralized with ammonia, and the thorium again precipitated by adding the same amount of hydrogen peroxide. This process was repeated 18 times. The final

[1] Proc. Chem. Soc., **18**, 120, (1902).

precipitate, which was reduced to a small amount through loss in precipitation , was carefully purified by Neish's method, and then ignited. Th X and subsequent products were removed by this treatment. The initial specific activity was 163, and the maximum, reached after about four weeks, was 377. It follows, therefore, that 18 precipitations with hydrogen peroxide do not completely remove radiothorium although the maximum activity has certainly been considerably reduced.

The thorium in a third portion of the nitrate solution was precipitated as thorium acetylacetonate by adding a slight excess of sodium acetylacetonate. The precipitate was washed with alcohol, dried, and then sublimed in a vacuum of 1 mm. of mercury. Portions of the sublimed salt from different parts of the tube were separately collected, and their activities measured. Three portions showed minimum specific activities of 167, 192 and 188, and maximum activities, one month later, of 444, 488 and 460 respectively.

A solution of thorium nitrate was precipitated fractionally with a solution of oxalic acid. The first of the eight fractions had a minimum activity of 208, and a maximum activity one month later of 476. The eighth fraction showed the same maximum activity.

In addition to these reactions, the thorium was precipitated, many times repeated, with such reagents as, potassium chromate, sodium thiosulphate, sulphuric acid in rather concentrated solution, etc. In a solution of thorium nitrate was precipitated repeatedly small amounts of barium sulphate by adding alternately barium chloride and sulphuric acid. Results differing but slightly from those given above were obtained in each case.

Some of the more important results are collected in Table XIV.

TABLE XIV.

| | $k_1$ min. | $k_1$ max. | $\frac{\text{min.}}{\text{max.}}$ |
|---|---|---|---|
| 100 precipitations with ammonia ..... | 185 | 435 | 2.35 |
| 18 " " hydrogen peroxide .... | 163 | 377 | 2.31 |
| Sublimation of the acetylacetonate ..... | 167 | 444 | 2.66 |
| Oxalic acid precipitation—1st fraction..... | 208 | 476 | 2.29 |
| " " " 8th " ..... | ... | 476 | .... |
| 8 precipitations with sodium thiosulphate..... | 190 | 482 | 2.54 |
| 7 " " potassium chromate .... | 196 | 494 | 2.52 |
| | | Mean | 2.45 |

While the experiments did not lead to the desired result—the complete separation of radiothorium from thorium—they serve to emphasize the remarkable persistancy with which radiothorium is retained by thorium. It seems to be a very easy matter to separate Th X and subsequent products, as shown by the experiments described, as well as by the earlier work of Moore and Schlundt.[1]

Two new papers by Hahn[2] are important in connection with the foregoing. Hahn finds that freshly made commercial samples of thorium are more active than older ones. The activity was smallest for samples three to nine years old. A sample twelve years old had greater activity. It is suggested in explanation that radiothorium has a period of about two years (a similar paper by Blanc[3] gives the period as 737 days), but that it is formed from an inactive product which is in turn the direct product of thorium. This intermediate product, called mezothorium, was isolated in an impure form by Hahn. It gives thorium emanation, and its activity increases steadily with time. The spontaneous loss of activity of commercial thorium is explained as due to the more or less complete removal of mezothorium in the process of preparation. Radiothorium and subsequent products then decay with time.

In Table XIV, it appears that the activity after the maximum amount of Th X has formed is in exery case appreciably less than the activity of sample A for which $k_1 = 513$. The small activity represents a smaller proportion of radiothorium and products than was present in sample A. The portion of the radiothorium lost may have been removed chemically, or it may have simply decayed in the time which elapsed between the preparation and measurement of sample A and the samples in question. An approximate calculation based on Blanc's value for the period of radiothorium indicates that all cases, excepting where the purification was by means of hydrogen peroxide, natural decay alone of radiothorium would account very largely for the dimunition of activity observed.

I have measured the activity of some samples of thorium dioxide which had been prepared and purified by Neish's method one and one-half years ago. The activity had decreased about 30 per cent. The decrease is less than that calculated by Blanc's value for the

[1] Jour. Phys. Chem., **9**, 682, (1905).
[2] Ber. d. chem. Ges., **40**, 1462 and 3304, (1907).
[3] Physik, Z., **8**, 321, (1907).

decay constant of radiothorium, assuming the total activity to be due to radiothorium and subsequent products, and that the rate of reformation of radiothorium is negligible. These results indicate that thorium alone is active. The activity of one gram of thorium freed from all its products is probably between 100 and 130. Further detailed experiments are necessary to determine with accuracy the activity of thorium when free from all its products.

## Part II.

### *Uranium Compounds.*

As has been already mentioned in connection with the thorium compounds, the investigations of McCoy[1] and Goettsch[2] showed that the total activity of one gram of uranium is independent of its form of chemical combination and is equal to 790 units, the unit being the observed activity of 1 sq. cm. of a thick film of the oxide, $U_3O_8$. The total activity associated with one gram of uranium in a mineral was found to be 3280 units. Minerals were therefore found to be 4.15 times as active as pure compounds of equal uranium content. Rutherford showed that the maximum ionization of a given substance is not produced if the distance between the electrodes is too small. This fact was completely explained by the work of Bragg and Kleeman,[3] who showed that the $\alpha$-rays of any radioactive substance have, in air, a definite range throughout which they produce ionization. Maximum ionization is produced only when the ionization chamber is sufficiently large to permit all the $\alpha$-rays to reach the limits of their ranges. The ranges of radium and its products[4] are between 3.50 and 7.06 cm., while that of uranium is probably near 3.5 cm.[5] The electroscope used by McCoy had the electrodes set at 3.5 to 4.5 cm. While these distances are doubtless great enough for pure uranium compounds, they are too small for the minerals the activity of which is due, in large measure, to radium and its products. The new experimental results, to be described, justify this conclusion. The activity of uranium in pure compounds was practically unchanged when measured with

[1] Loc. cit.
[2] Loc. cit.
[3] Phil. Mag., **10**, 318 and 600, (1905).
[4] See also Bragg, Phil Mag., **8**. 726, (1904).
[5] Bragg, Phil. Mag., **11**, 754, (1906).

electrodes at a distances of 8.5 cm., while under the new conditions of measurement, the activity of a mineral was about 4.0 per cent. greater.

The recent work on the range of the $\alpha$-rays also served to indicate another possible error in the method of McCoy. According to this method, films of the active material were deposited in flat, circular metal dishes 7.02 cm. in diameter with rims 0.8 cm. high.[1] Inasmuch as the solid angle subtended by the rim, with any point of the film as centre, was the same for all films, the rims being of equal height, it was thought at first that the same fraction of the radiation would be cut off by the rims in all cases.[2] However, films sending out $\alpha$-rays with greatest effective range will suffer greatest loss of activity on account of the rims. Experiment confirmed this supposition, although the difference in percentage loss was not great. Thus, while the actual dimunition of the activity due to the rims was 8.2 per cent, for uranium oxide, the corresponding decrease in activity in the case of uranium minerals amounted to 8.8 per cent., a difference of 0.6 per cent.

Finally, in order to obtain exact results, the observed activity of a film of a uranium ore must be corrected for the activity of the emanation which is lost spontaneously. Boltwood[3] has determined the percentage of emanation thus lost for a large number of uranium minerals and has found appreciable loss in every case.

*Experimental part,— the effect of insufficient ionization space.*

In order to obtain results free from the above mentioned errors, a new series of determinations was undertaken. A new electroscope was constructed for the activity measurements. It was made of sheet brass, 1.4 mm. thick, and consisted of two superimposed rectangular compartments, a smaller upper one 7.5 x 10 cm. and 12.5 high, which contained the gold leaf system, and a larger lower one 19.5 cm. square and 14 cm. high, which constituted the ionization chamber. The circular brass plate which served as the upper electrode had a diameter of 14 cm. The film, whose activity was to be measured, was placed on a movable support in the lower part of the ionization chamber and so arranged that the distance between the film and the charged electrode could be changed at will. The gold

[1] Tin plate jelly-glass covers were used.
[2] Goettsch, J. Am. Chem. Soc., **28**, 1548, (1906).
[3] Phil. Mag., [6], **9**, 599, (1905).

leaf-system was connected with the electrode by a brass rod which passed through an insulating amber support. The motion of the gold leaf was observed by a micrometer microscope, the upper compartment being provided with glass windows. The whole instrument was surrounded by a wooden case to guard against any sudden changes in the temperature, or effect of air currents. To charge the electroscope a difference of potential of about 450 volts was required.

In order to determine the effect due to insufficient ionization space in the electroscope previously used, a series of films of Pitchblende No. 1 were prepared in the same way as described for sample A of thorium dioxide. The activity of the films was then measured in the electroscope with the charged plate placed first at a distance of 4.5 cm. from the active film, and then at a distance of 8.5 cm. With the plate placed at the latter distance, the ionization space in the electroscope is sufficient to permit all the $\alpha$-rays given off by the mineral to reach the end of their free paths before being stopped by the charged plate, or by the walls of the electroscope. For these measurements the films were deposited as usual in tin dishes with rims. These dishes were 7.02 cm. in diameter, and 0.8 cm. high. On making the two sets of measurements, and calculating the specific activity of the ore from the results obtained, it was found that with the plates only 4.5 cm. apart the activity indicated was 4.0 per cent. too low. Accordingly all subsequent measurements were made with a distance between the plates of 8.5 cm.

*On the effect due to the rims.*

To determine the effect due to the rims, a series of films of pure uranium oxide were made in the ordinary dishes with rims 0.8 cm. high and their activities measured. The rims were then carefully cut off with a pair of snips. The thick film used as standard was likewise measured first with the rim on, and then after it had been cut off. It was found that the specific activity of the oxide, as calculated from the measurements made with the rims on, was 8.2 per cent. less than the corresponding value obtained with the rims off.

Films were also made of three uranium ores in the same way as for the pure oxide. The ores were carefully sampled, and special care was taken when preparing the films to prevent any segregation of the more active constituents. Activity measurements were made first with the rims on, and then after they had been cut off. It was

found, as in the case of the pure oxide, that the specific activity of each of the minerals, as calculated from the measurements made of films with rims, was less than the corresponding value obtained when the films were measured without rims. The average decrease in activity due to the rims for the three minerals amounted to 8.8 per cent. The corresponding value obtained for the pure oxide was 8.2 per cent.

All films subsequently prepared were therefore deposited on perfectly flat surfaces. This was most conveniently done by placing false bottoms made of sheet copper in the vessels previously used. The proper amount of the finely powdered material to be used in making a film was then vigorously shaken up with alcohol in a small beaker and quickly poured into one of the dishes in the usual way. When the alcohol had evaporated, the material was left deposited on the false copper bottom which could then be removed, weighed, and its activity determined. The diameter of each copper plate was 7.00 cm.

*The specific activity of uranium in uranium oxide.*

In Table XV, is given the results obtained when a series of films of pure uranium oxide was made on flat copper plates in the way described. The standard of activity used was a thick film of the oxide weighing about 0.025 gram per sq. cm., and deposited on a copper plate of the same area as the others. The activity of 1 sq. cm. of such a film was taken as unit activity. The significance of the symbols is the same as already given in the description of the thorium compounds.

TABLE XV.—*Uranium oxide, $U_3O_8$*

| $w$ | $a$ | $\frac{w}{a}$ |
|---|---|---|
| .6040 | 38.7 | .01560 |
| .2902 | 36.5 | .00795 |
| .2054 | 33.1 | .00621 |
| .1048 | 23.0 | .00455 |
| .0757 | 18.7 | .00404 |
| .0534 | 14.6 | .00365 |

$$\left(\frac{w}{a}\right)_0 = .00296$$

Since $k_1 = 2/\left(\frac{w}{a}\right)_\infty$, the true specific activity of uranium oxide in terms of the activity of 1 sq. cm. of a thick film of the oxide is $\frac{2}{\cdot 00296} = 676$. Uranium oxide contains 84.85 per cent. of uranium. Therefore, the true total activity of 1 gram of uranium in uranium oxide is $\frac{676}{\cdot 8485} = 796$ units.

*Uranium ores,—Method of analysis.*

A series of experiments was likewise undertaken to determine the total activity of uranium in its ores. The ores investigated were powdered and then ground up finely in an agate mortar with alcohol to prevent the possible loss of any highly radioactive dust. The ground ore was then thoroughly mixed by sampling, and analyses made for uranium and thorium. The same sampled portion of ore was likewise used in making films, and in determining the amount of emanation spontaneously evolved.

The method adopted in determining the percentage of uranium in its ores is a modification of that of Brearly.[1] The method of procedure is essentially the same as that employed by Boltwood,[2] but, as no satisfactory results could be obtained when using most of the reagents in the proportions which he directed, a number of experiments were undertaken to determine to what extent the method should be modified. Satisfactory results were finally obtained when the analyses were carried out as follows:—About .3 gram of the finely ground ore was dissolved in dilute hydrochloric acid with a little nitric acid added; the solution was evaporated to dryness, moistened with a little concentrated hydrchloric acid and again evaporated, this being repeated three times to render the silica insoluble. The solution was then taken up in dilute hydrochloric acid and the insoluble residue filtered off. Hydrogen sulphide was passed into the filtrate for an hour, the precipitated sulphides filtered off, and after boiling to remove the excess of hydrogen sulphide, the salts in solution were oxidized by adding a little bromine water. On boiling a short time, a little more bromine water was added, and the boiling continued until the excess of bromine was driven off. The solution was allowed to cool some-

[1] Loc. cit.
[2] Phil. Mag., [6], **9**, 603, (1905).

what, .2 gram of microcosmic salt added, and then poured into a solution of 30 grams of sodium carbonate (crystals) in 125 cc. of water. The mixed solutions, which should not have a volume exceeding 300cc, was boiled gently for five minutes, allowed to cool somewhat, 20 grams of ammonium chloride added, and the boiling repeated as before for five minutes. After allowing to stand for some hours, the clear solution was decanted off, and the precipitate washed. The filtrate was boiled in a large beaker until the ammonium carbonate was driven off, and the uranium phosphate precipitated from the solution. 10 cc. of dilute nitric acid was added to the hot solution and the boiling continued until the uranium phosphate again dissolved. In the case of most ores, an insoluble residue was found to remain after the uranium had all gone into solution. This was filtered off, and the filtrate evaporated to 200cc. After allowing to cool, .8 gram microcosmic salt was added, and then 10 grams of crystallized sodium thiosulphate. The solution was heated very carefully to boiling, and boiled gently for 15 minutes, allowed to stand for a short time, the precipitated sulphur and uranium phosphate then filtered through a platinum Gooch crucible, washed, dried for an hour in the air bath, and then ignited to burn off the sulphur. The residue was dissolved in as small amount as possible of concentrated nitric acid, the asbestos filtered off, and ammonia added until a precipitate began to form. The solution was then heated on the water bath and just enough nitric acid added until the solution became clear again. After allowing to cool, it was poured into a concentrated solution of 25 grams of ammonium carbonate in 100 cc. of water. Hydrogen sulphide was passed in for 15 minutes, and, after heating to boiling, it was allowed to stand for a few hours. The slight precipitate formed was filtered off, the filtrate boiled to drive off excess of ammonium corbonate, 10 cc. of dilute nitric acid added, and then, on allowing to cool, .8 gram of microcosmic salt and 10 grams of sodium thiosulphate. The solution was boiled for 15 minutes as before, filtered through a Gooch crucible, washed, dried for an hour in the air bath at 110°, the sulphur carefully burned off and the residue then heated to low redness for 15 minutes. The uranium may be determined from the weight of the phosphate thus obtained. It was found more satisfactory, however, to dissolve the residue in 100 cc. of dilute sulphuric acid, reduce with zinc, and then titrate

with a standard solution of potassium permanganate.[1] The permanganate solution was standarized first by means of pure iron wire, and then by titrating a weighed amount of uranium oxide, $U_3 O_8$, dissolved in sulphuric acid and reduced with zinc. Both results were found to agree exactly.

Table XVI gives the locality of origin, and percentage of uranium in the three minerals analysed. All were analysed for thorium by Neish's[2] method, 5 gram portions of each ore being taken for analysis, but no trace of thorium was found in any case. Since it has been shown that the ratio of the activity of a mineral to its uranium content is constant, it was not considered necessary to investigate any large number of minerals in order to determine the true value of this ratio.

TABLE XVI.

| Mineral. | Locality. | Per cent. of Uranium. |
|---|---|---|
| Pitchblende, No. 1 | Unknown | 44.7 |
| " No. 2 | Central City, Col | 54.0 |
| " No. 3 | Gilpin Co., Col | 58.1 |

*The observed specific activity of the minerals.*

A series of films was made of each mineral in the same way as for the pure uranium oxide. In the last column of Table XVII is given the *observed* specific activity for each mineral.

TABLE XVII.

| Mineral. | $\left(\frac{w}{a}\right)_o$ | $k_1$ (uncorrected) |
|---|---|---|
| Pitchblende, No. 1 | .001264 | 1582 |
| " No. 2 | .001048 | 1908 |
| " No. 3 | .000991 | 2018 |

*Determination of evolved emanation.*

In order to determine the *true* specific activity of the minerals and the correct value of the ratio of the activity of the minerals to that of the pure oxide containing the same amount of uranium, the observed activity of each mineral must be corrected for the loss of

[1] Goettsch, J. Am. Chem. Soc., **28**, 1547, (1906).
[2] Loc. cit.

the evolved emanation, as was already stated. The emanating power of each mineral was determined separately. For this purpose a portion of the ore, ground to the same degree of fineness as that subsequently used in determining the retained emanation, was carefully weighed and introduced between plugs of cotton wool in a straight calcium chloride tube. A slow current of air was then drawn through the tube for 10 minutes to remove any emanation which might be clinging to the solid particles. The tube was then tightly stoppered, and allowed to stand for a month. At the end of this time, the evolved emanation which had collected was removed by drawing slowly through the tube about 250 cc. of air. This was collected in a flask, allowed to stand 15 minutes, and then introduced into the gas electroscope which had previously been exhausted by a water pump. At the end of two hours, it was found that the activity of the gas in the electroscope had reached a value remaining constant for a considerable length of time. Accordingly, in every case, the emanation was allowed to stand in the electroscope two hours before noting its activity. The observed activity, divided by the weight of the ore taken, gives the activity of the emanation lost by one gram of the mineral.

*Determination of retained emanation.*

To determine the activity of the emanation retained by the ore, a weighed portion, about .03 gram, was placed in a small flask, treated with a mixed solution of 20 cc. dilute nitric acid and 5 cc. of dilute sulphuric acid. The small flask was connected with a liter flask filled almost to the neck with water to which was added a few cc. of a sodium hydroxide solution. This flask was in turn connected by means of a siphon with a third vessel. On heating the solution in the small flask to boiling, the ore was decomposed, and the gases and steam carried the emanation over into the liter flask, displacing the water. The boiling was continued 10 minutes. The liter flask containing the solution was then tightly stoppered and allowed to stand 15 minutes to permit of the decay of the actinum emanation. The inclosed gas was then introduced into the electroscope as before, and the activity noted at the end of two hours. The activity due to the emanation retained in 1 gram of the ore, as thus determined, plus the activity of the evolved emanation as previously found, gives the total activity of the emanation in 1 gram of the substance.

The following Table gives the values found, and the per cent. of the emanation spontaneously lost by each mineral. The activities are given in terms of the fall of the leaf in scale divisions per second. Each number represents the mean of three determinations all of which agreed closely. The values in the second, third and fourth columns refer to 1 gram of the ore.

TABLE XVIII.

| Mineral. | Activity of retained emanation. | Activity of evolved emanation. | Activity of total emanation, ($a$) | Per cent of total emanation evolved. | Amount of U in 1 gram of ore, ($P$). | $\frac{a}{P}$ |
|---|---|---|---|---|---|---|
| Pitchblende No. 1. | ·629 | ·0246 | ·654 | 3·76 | ·447 | 1·46 |
| " No. 2. .... | | ·0649 | ·786 | 8·25 | ·540 | 1·456 |
| " No. 3. | ·800 | ·0369 | ·837 | 4·41 | ·581 | 1·44 |

The last column of Table XVIII shows that the activity of the total emanation is strictly proportional to the percentage of uranium in the mineral. This is in agreement with the results found by Boltwood.[1]

When the amount of retained emanation in ore No. 2 was determined in the way described, it was found that the amount obtained was less than was expected when compared with the results obtained for the other two ores. A comparatively large residue was left when this ore was treated with the mixed solution of nitric and sulphuric acids. A small portion, about .06 gram, was then weighed out in a platinum crucible. About 4 grams of potassium acid sulphate, which had been heated to quite fusion, was poured into the crucible containing the ore, and the heating continued until the ore had completely dissolved. On cooling, the fused mixture was dissolved in acidified water, boiled for five minutes to drive off all emanation, and then sealed up in a small flask. After standing for four days, the emanation was again boiled off, collected in the usual way, and its activity observed. The radium emanation reaches half its equilibrium amount in four days. Hence, twice the activity observed, divided by the weight of the ore taken, gives directly the activity of the total emanation in 1 gram of the ore. The value thus obtained, .786, must represent the true activity of the total emanation for ore No. 2, since it was brought into complete solution by the fusion with potassium acid sulphate. As the value obtained by

[1] Phil. Mag., [6], 9. 599, (1905).

treatment with the mixed acid solution was much less than this, it follows that all the emanation can not always be expelled from an ore by boiling with an acid solution only.

*The percentage loss of activity of a uranium mineral due to the evolved emanation.*

It is probable that the emanating power of a compact mineral like Pitchblende is negligibly small until the mineral is powdered. If so, the loss of activity must date from the time when the mineral is pulverized. During a few weeks, or even months, after pulverization, loss of emanation will therefore cause an appreciable deficiency in the amount of the products of rapid decay, namely RaA, RaB and RaC only; while the amount of RaD, which has a period of about 40 years, will not be noticeably altered. The amounts of RaE and RaF, which are products of RaD, will also be unchanged by loss of emanation. In order that one may know by what fraction the specific activity of a mineral is decreased by the spontaneous loss of emanation after pulverization, it is necessary to know what fraction of the total activity is due to the emanation and the products RaA, RaB and RaC. The experimental determination was made as follows:—A portion of ore No. 1, finely ground, was treated with nitric acid, evaporated to dryness, and the process repeated three times at intervals of two hours to admit of the decay of the radium products of short period. After the third evaporation, the residue was heated just strongly enought to decompose the nitrates present. The resulting oxides were then ground up finely in alcohol. The alcohol was evaporated off on a water bath. The fine powder remaining was made into films as quickly as possible, and their activities determined in the usual way. The mean of two experiments gave for the specific activity of the ore, when thus treated, a value of 51.5 per cent. less than the original value. Since, by this treatment, all the emanation originally retained by the ore, as well as the products of short period, was removed, it follows that the activity due to the radium emanation, and its products RaA and RaC, is equal to approximately one-half of the total activity of the ore.

The relative activity due to the emanation, RaA, RaB and RaC, may also be calculated from theoretical considerations. Boltwood[1]

[1] Am. J. Sci., **21**, 413, (1906).

has shown by direct experiment that the activity of RaEm+RaA+RaB+RaC is 4.64 times as great as that of the equilibrium amount of radium. His experiments also indicate, as he has pointed out, that the activity of the equilibrium amount of any member of a radioactive series is proportional to its range. The range of the $\alpha$-rays of RaF is 3.85 cm., while that of radium is 3.50 cm. Consequently, RaF is $\frac{3{\cdot}85}{3.50} = 1.10$ times as active as the equilibrium amount of radium. Since RaD is inactive, and RaE gives only $\beta$-rays, the activity due to the Em + RaA + RaB + RaC = $\frac{4{\cdot}64}{6{\cdot}74}$ times that of radium and all its products. Now, uranium minerals are 4.54 times as active as pure compounds of equal uranium content, as will be shown below. Therefore, radium and its products are $(4.54 - 1) = 3.54$ times as active as the equilibrium amount of uranium. Consequently, the activity of RaEm+RaA+RaB + RaC = $\frac{4{\cdot}64 \times 3{\cdot}54}{6{\cdot}74 \times 4{\cdot}54} = 0.536$ of the total activity of a mineral. This amount, 53.6 per cent., agrees fairly well with that found by direct experiment which gave 51.5 per cent. We may therefore consider that the percentage loss of activity due to lost emanation of a uranium mineral, which has been in the powdered state not more than a few months, is equal to one-half of the emanation evolved.

*The specific activity of uranium in minerals.*

The proper corrections may now be applied to the observed specific activities of the ores as given in Table XVIII. Table XIX gives a summary of the results obtained.

TABLE XIX.

| Ore. | $k_1$ (uncorrected). | Per cent. of Em. evolved. | Per cent. of activity lost by evolved Em | Per cent. of activity remaining. | $k_1$ (corrected). | Amount of U in 1 gram of ore, (P). | $\frac{k_1}{P}$ |
|---|---|---|---|---|---|---|---|
| No. 1 ..... | 1582 | 3.76 | 1.9 | 98.1 | 1613 | .447 | 3610 |
| No. 2 ..... | 1908 | 8.25 | 4.1 | 95.9 | 1990 | .540 | 3685 |
| No. 3 ..... | 2018 | 4.41 | 2.2 | 97.8 | 2064 | .581 | 3552 |

Mean = 3616

The number 3616 represents the true specific activity of uranium in its ores. The corresponding value for the activity of uranium in its pure compounds is 796. Therefore, the true ratio of the

activity of uranium minerals to the pure compounds containing the same amount of uranium is $\frac{3616}{796} = 4.54$.

*The specific activity of thorium in minerals.*

The activity of the thorium films in the first part of this paper was measured in an electroscope having a distance between the plates of only 4.5 cm. All measurements were made, moreover, without the rims being removed from the tin dishes in which the films were deposited. Two sources of error were thus introduced in the calculation of the total activity of thorium, as the work on uranium has shown. Since the percentage error due to these sources is a constant one, or approximately so, this had no important effect on the chief object of the research which showed that the specific activity of thorium in its minerals is constant, while in its commermercially prepared compounds it has a variable activity much less than this. As the specific activity of thorium in its minerals is constant, it was not considered necessary to repeat the measurements of more than three of the minerals in order to determine the true value of this constant. The large electroscope already referred to in connection with the uranium minerals was used. The distance between the plates was 8.5 cm. The rims were removed from the films before measuring their activities. Table XX which corresponds to Table XIII, gives a summary of the results obtained. The new value found for the total activity of 1 gram of uranium in its ores—3616 units—was used in calculating the activity due to the uranium in each thorium mineral.

TABLE XX.—*Thorium minerals.*

| Name. | %Th | %U | $\left(\frac{w}{a}\right)_0$ | $k_{1m}$ | $k_{1U}$ | $k_{1Th}$ | $\frac{k_{1Th}}{P_{Th}}$ |
|---|---|---|---|---|---|---|---|
| Orangite ... | 43.1 | 7.76 | .00283 | 707 | 281 | 426 | 990 |
| Thorite .... | 46.6 | 6.26 | .00286 | 699 | 226 | 473 | 1015 |
| Monazite .. | 15.18 | .46 | .01160 | 172 | 16.6 | 155.4 | 1025 |

Mean = 1010

The mean of the numbers given in the last colum is 1010. This represents the true total activity of 1 gram of thorium in its ores.

This investigation was carried out under the direction of Professor H. N. McCoy, and I take much pleasure in expressing my indebtedness to him for his many valuable suggestions and kind supervision during the progress of the work.

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